Ellipsometry
X-ray reflectivity

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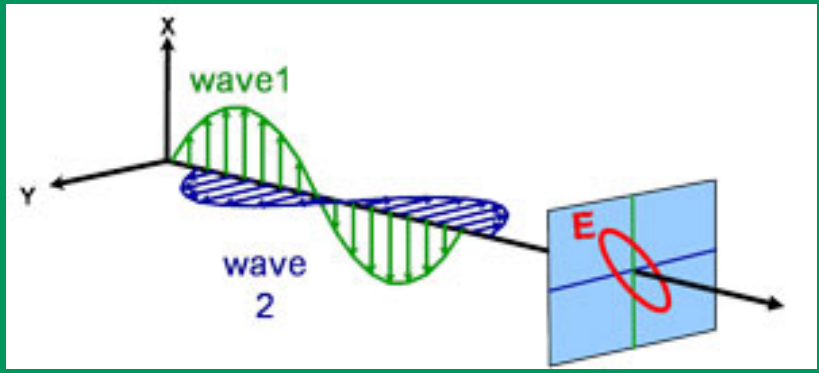
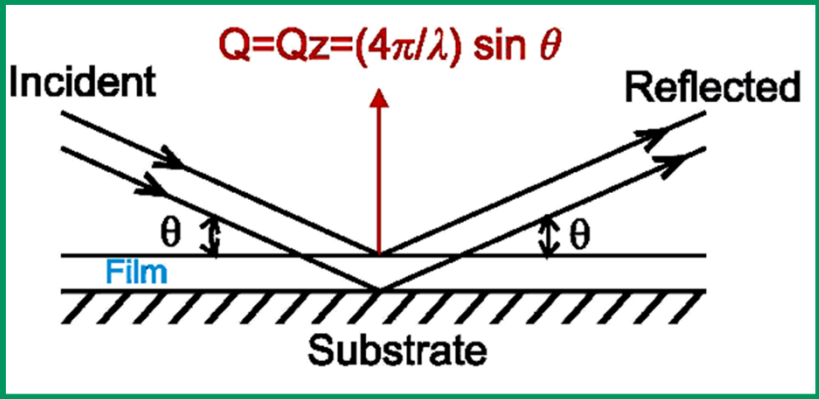
CHEM-L2000

Eero Kontturi

4th March 2024





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Learning objectives

- To roughly understand the principles of ellipsometry and XRR
- To be aware of their applications and restrictions when analysing polymeric (soft) materials
- To be able to point out what kind of information one can gain from applying ellipsometry and XRR on soft materials

Outline

(1) General aspects of both techniques

(2) Ellipsometry
- theory
- measuring / interpreting
- applications

(3) X-ray Reflectivity (XRR)
- theory
- measuring / interpreting
- applications

Important requirements

- Both ellipsometry and XRR are analytical techniques for *supported ultrathin films*
- The substrate (support) must reflect light (ellipsometry) or X-rays (XRR)
- Free-standing films (without a reflecting substrate) *cannot* be analyzed by either of the techniques

General applications

- Both ellipsometry and XRR are generally used for inorganic ultrathin films (hard materials)
- Soft, organic materials like natural polymers are less frequently analyzed and the interpretation methods for inorganic materials do not necessarily work for organic materials

Ellipsometry

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General considerations

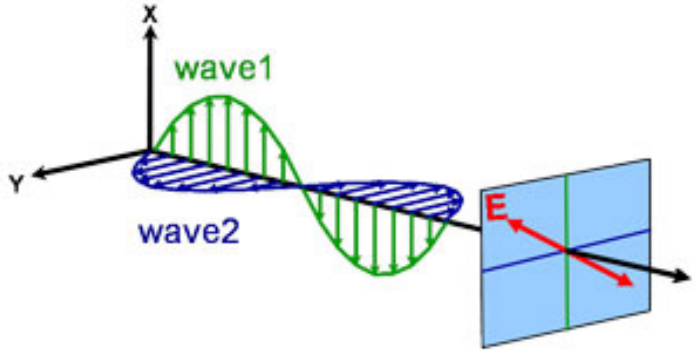
- Ellipsometry analyzes the dielectric properties of a supported ultrathin film
- Usually, film thickness and/or optical constants (like refractive index) are qualities measured with an ellipsometer

Theory: polarization

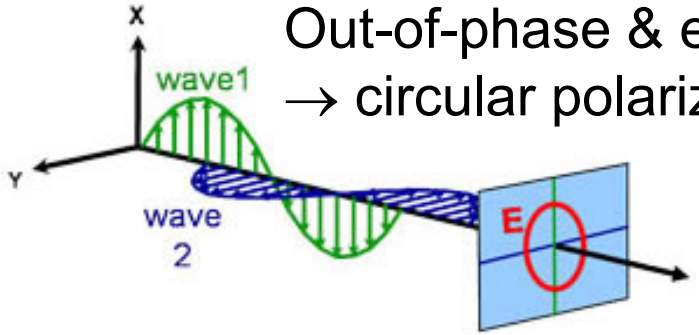
- Electric field of an electromagnetic wave is always perpendicular to its direction
- Polarized light: electric field follows a specific path with a distinct shape at any point

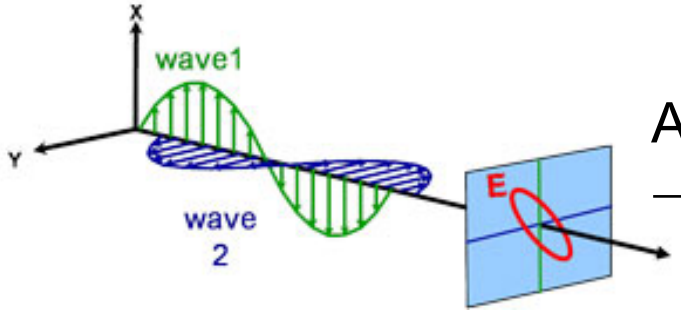
Two orthogonal light waves travelling at z-direction:

In-phase & different in amplitude
→ linear polarization



Out-of-phase & equal in amplitude
→ circular polarization

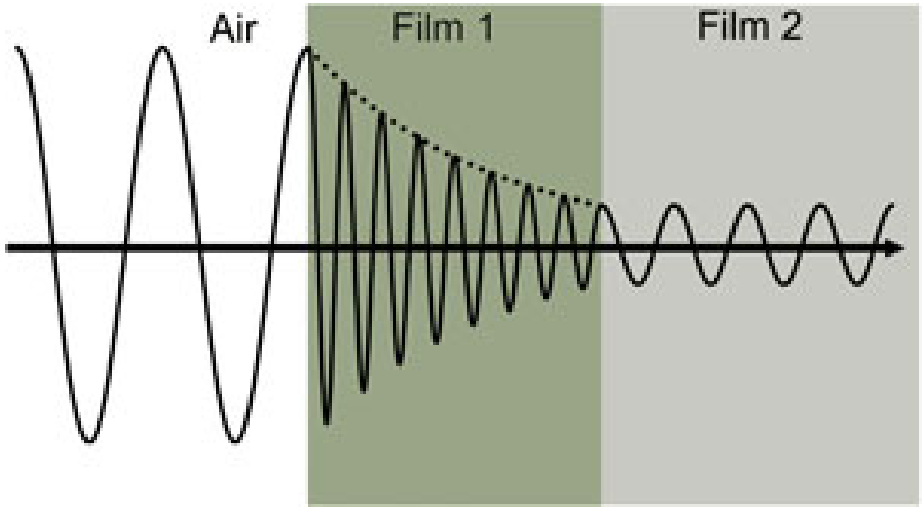




Arbitrary amplitude & phase
→ ellipsoidal polarization

Theory: interaction between light and material

- Light slows when it becomes in contact with material
- Because the energy of light stays the same, its frequency increases and, therefore, the wavelength decreases



Complex refractive index:

$$\tilde{n} = n + ik$$

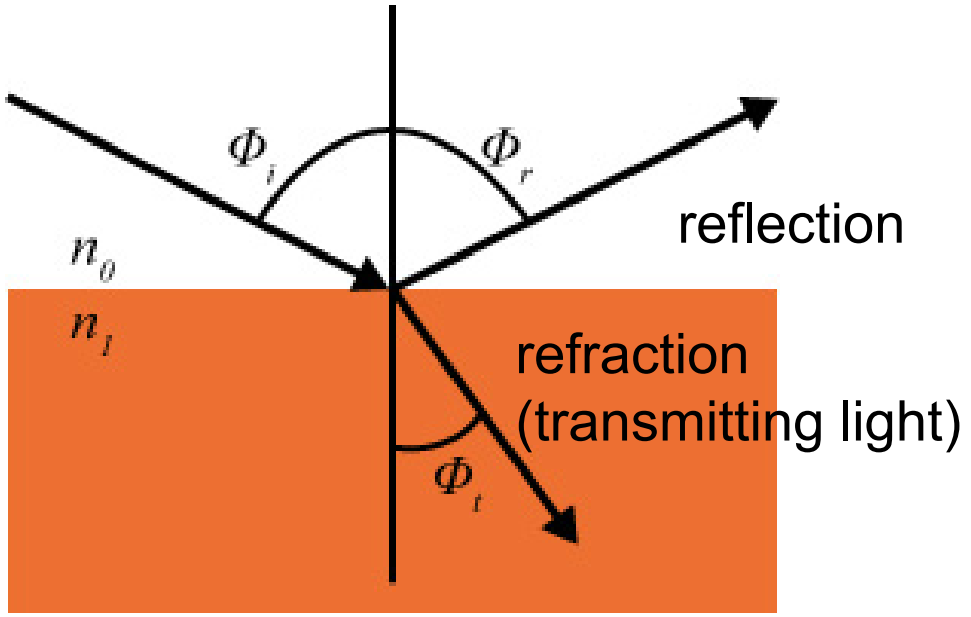
n – refractive index
k – extinction coefficient

Theory: interaction between light and material

At an interface, part of the light reflects and the remained transmits and refracts.

Snell's law: $n_0 \sin(\Phi_i) = n_1 \sin(\Phi_t)$

The mathematical expression of the phenomena of reflection/refraction is simple.

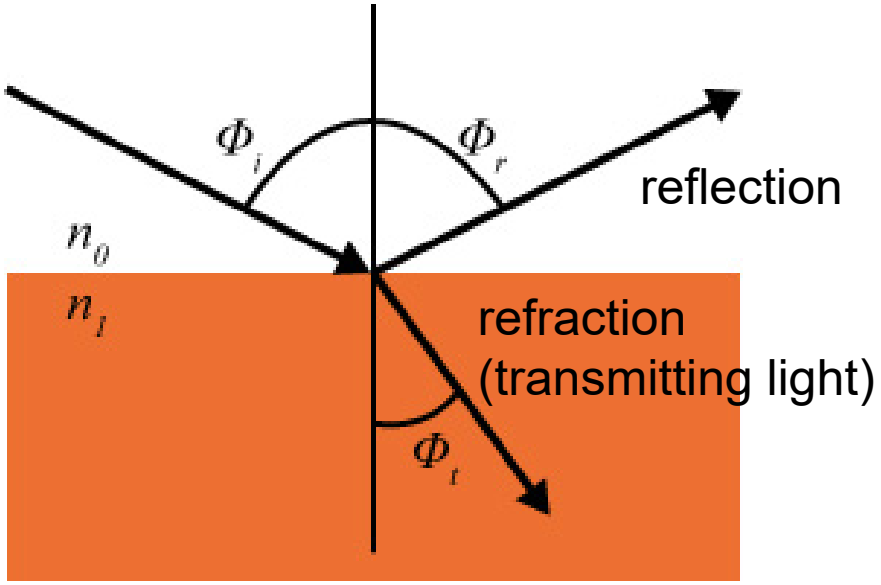


Theory: interaction between light and material

In terms of wave mechanics, the mathematical expression is more complex.

Snell's law:

$$n_0 \sin(\Phi_i) = n_1 \sin(\Phi_t)$$



Fresnel equations

$$r_s = \left(\frac{E_{0r}}{E_{0i}}\right)_s = \frac{n_i\cos(\Phi_i) - n_t\cos(\Phi_t)}{n_i\cos(\Phi_i) + n_t\cos(\Phi_t)}$$

$$r_p = \left(\frac{E_{0r}}{E_{0i}}\right)_p = \frac{n_t\cos(\Phi_i) - n_i\cos(\Phi_t)}{n_i\cos(\Phi_t) + n_t\cos(\Phi_i)}$$

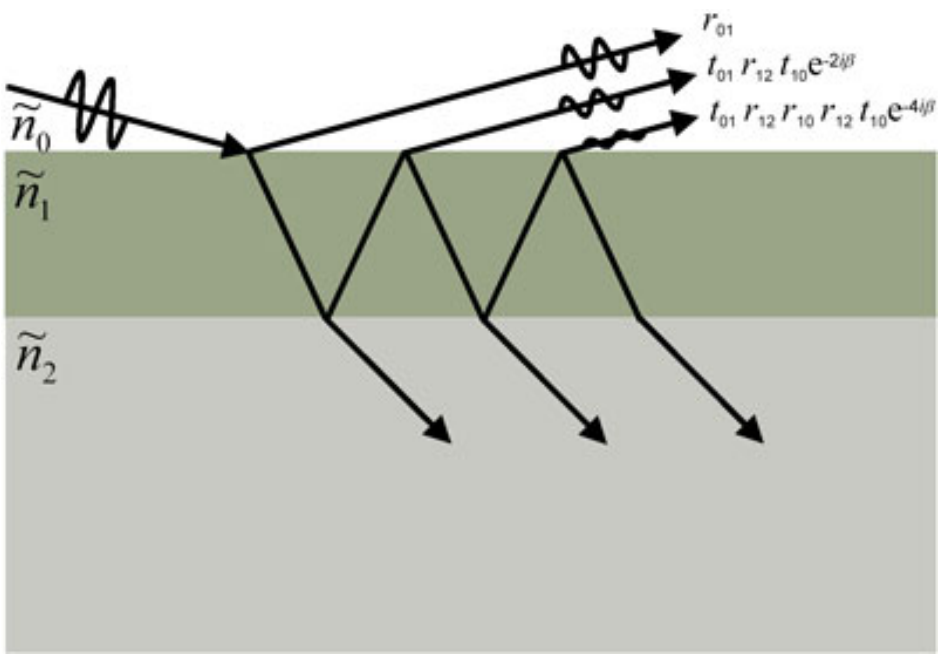
$$t_s = \left(\frac{E_{0t}}{E_{0i}}\right)_s = \frac{2n_i\cos(\Phi_i)}{n_i\cos(\Phi_i) + n_t\cos(\Phi_t)}$$

$$t_p = \left(\frac{E_{0t}}{E_{0i}}\right)_p = \frac{2n_i\cos(\Phi_i)}{n_i\cos(\Phi_t) + n_t\cos(\Phi_i)}$$

r – reflectance; t - transmittance
p – parallel; s – perpendicular
E – electric field

Theory: interaction between light and material

In terms of wave mechanics, the mathematical expression is more complex.



Fresnel equations

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r – reflectance; t - transmittance
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Measurements

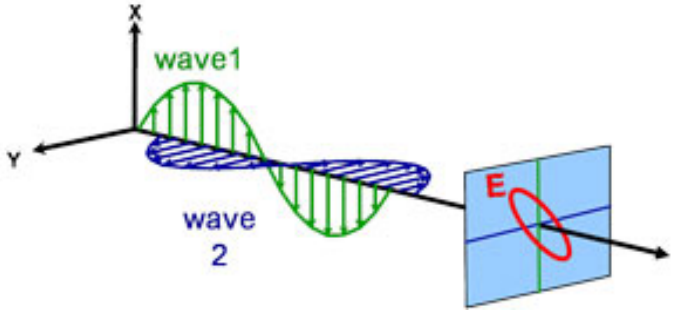
Ellipsometry actually measures the complex reflectance ratio (ρ), which can be denoted also as the ratio of the amplitudes of p (parallel) and s (perpendicular) components after reflection (r_p/r_s) :

$$\rho = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta}$$

$\tan(\psi)$ – amplitude ratio upon reflection
Δ - phase shift upon reflection

Change in polarization upon reflection

Remember



arbitrary amplitude & phase
→ ellipsoidal polarization

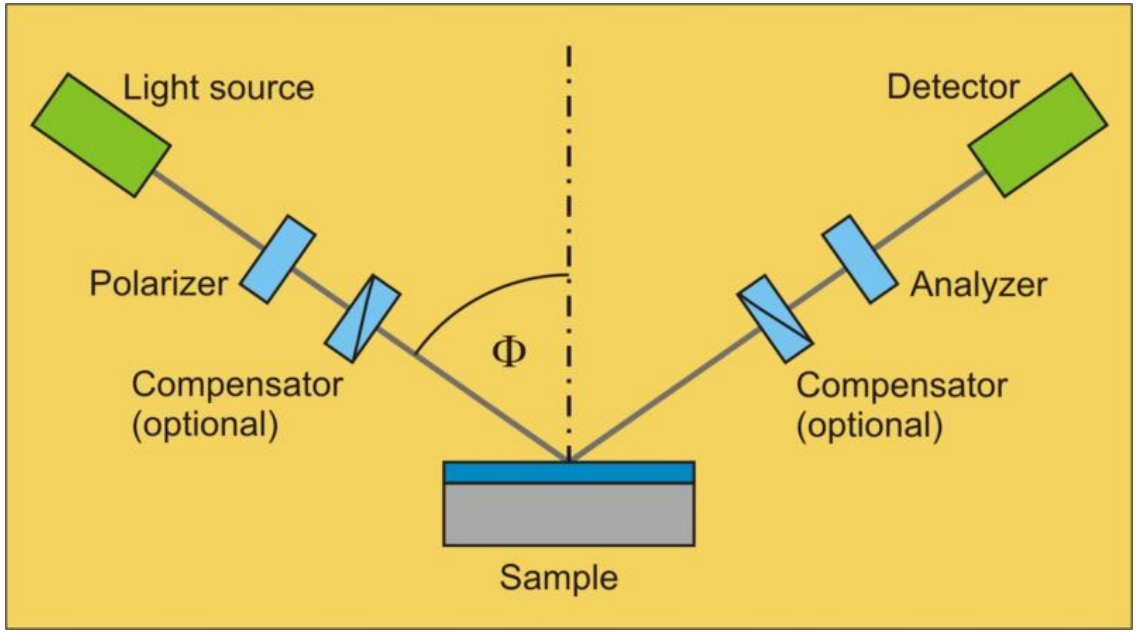
Interpretation of data

- Ellipsometry is an indirect method
- Reflectance ratio (r_p/r_s) does not yield any concrete physical information on the sample
- Modelling is required to yield actual physical values

→ One must iterate values for k (extinction coefficient) and n (refraction coefficient) which would give a reasonable fit to the measurement values

→ Values for film thickness

Experimental setup



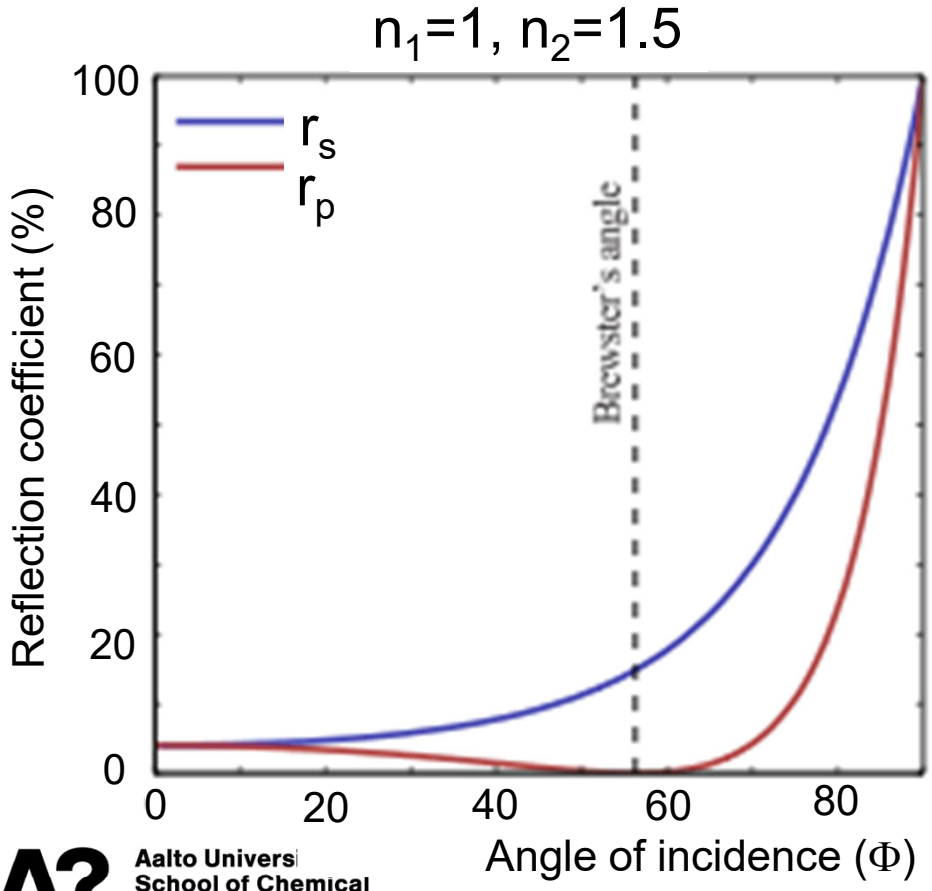
In a conventional ellipsometry measurement mode:

- monochromatic wavelength is used
- incident angle (Φ) is varied manually by a goniometer

(Spectroscopic ellipsometry is based on varying the wavelength of light)

Interpretation of data

The actual data that you get out of an ellipsometry measurement is the reflection coefficient as a function of angle of incidence for s- and p-components.



Reflectance coefficient is the ratio of light that has reflected from the sample, i.e., that has not been transmitted:

$r_s=1-t_s$
$r_p=1-t_p$

Note: when p-component is zero, the angle is called *Brewster's angle*.

Interpretation of data

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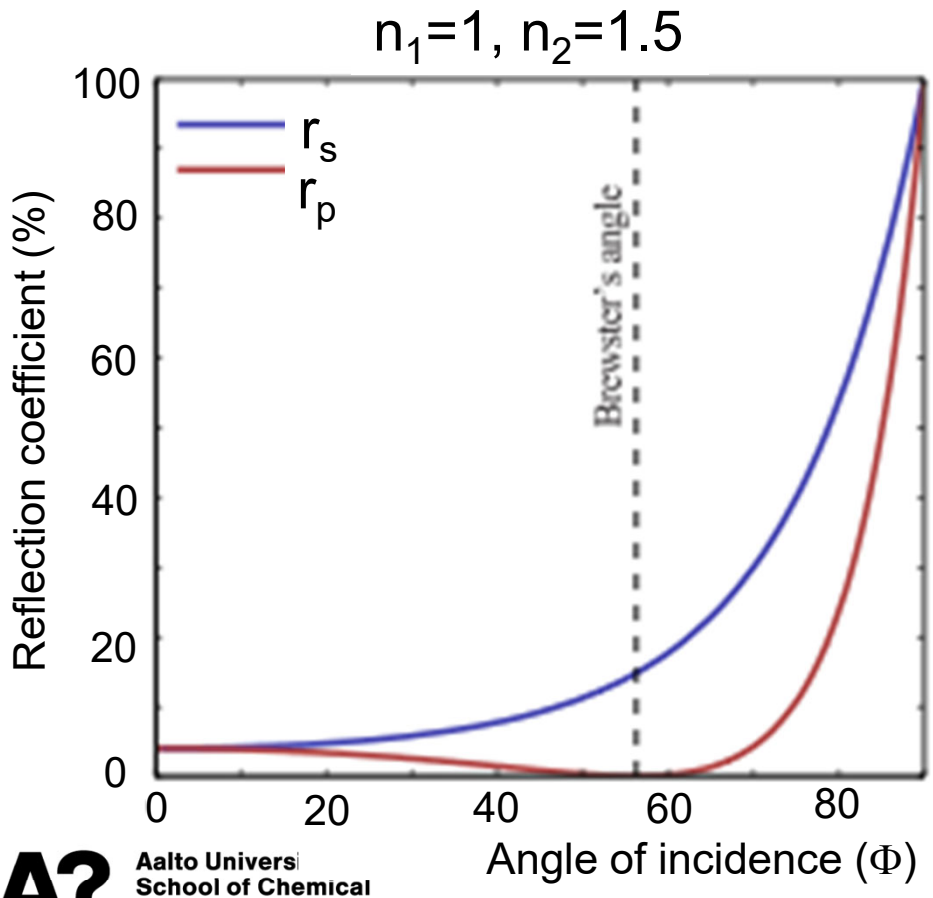

$$n_0 \sin(\Phi_i) = n_j \sin(\Phi_j)$$

$$\hat{n} = n + ik$$

n – refractive index
k – extinction coefficient

Modelling: n and k values are iterated to simulate the reflection curve with Fresnel equations.

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Interpretation of data

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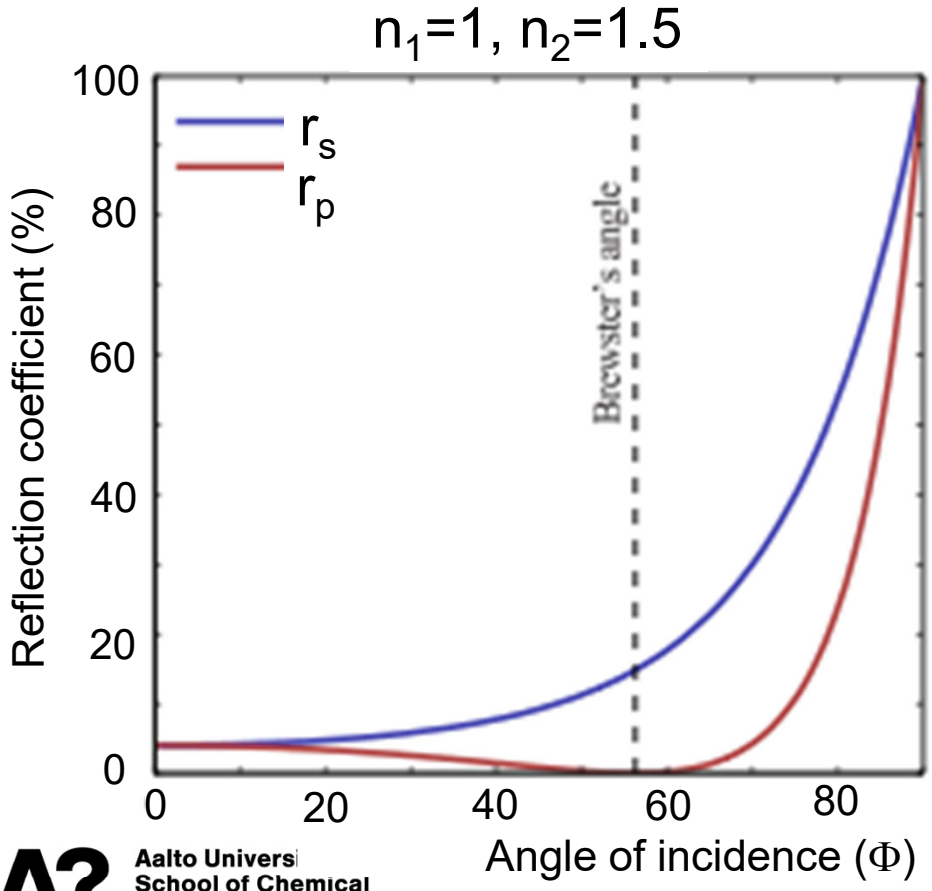

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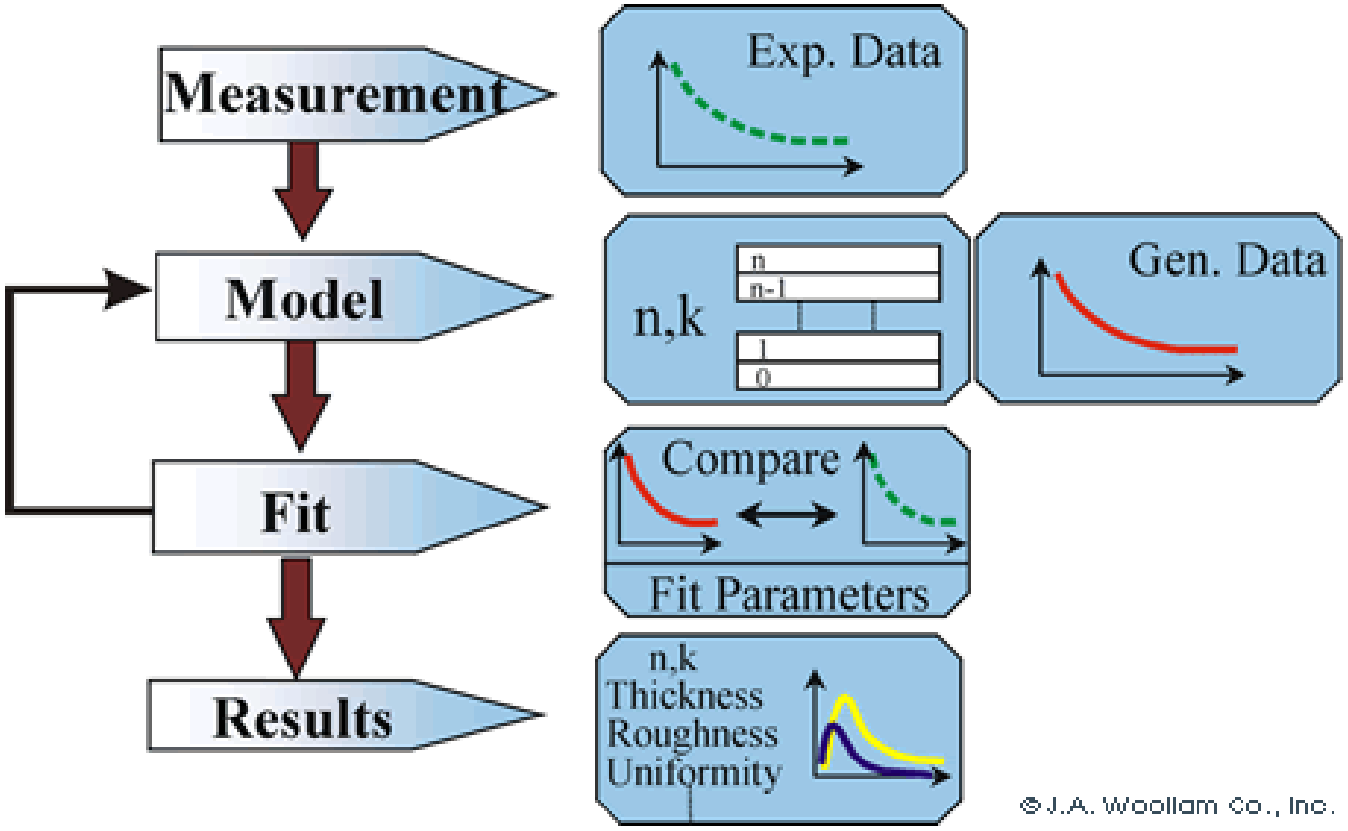
r – reflectance; t - transmittance
p – parallel; s – perpendicular
E – electric field

Interpretation of data



Important practical notions

- Probably the most common use of ellipsometry is to determine the film thickness
- Film thickness can be probed from a submonolayer (<nm) thickness to several micrometers
- It helps if you know what you are measuring: if you know the refractive index (n) of the film material, you only have to iterate the k-value
  $\rightarrow$ more reliable modelling of the reflectivity graph
  $\rightarrow$ more reliable film thickness value

Application example: *in situ* determination of enzyme activity

- Cellulase enzymes degrade cellulose into sugars
- Mechanisms of degradation are complex and difficult to interpret

→ Ultrathin model films can provide clarification to degradation mechanisms

- The enzymes first adsorb on cellulose, after which degradation begins
- This can be followed with in situ ellipsometry

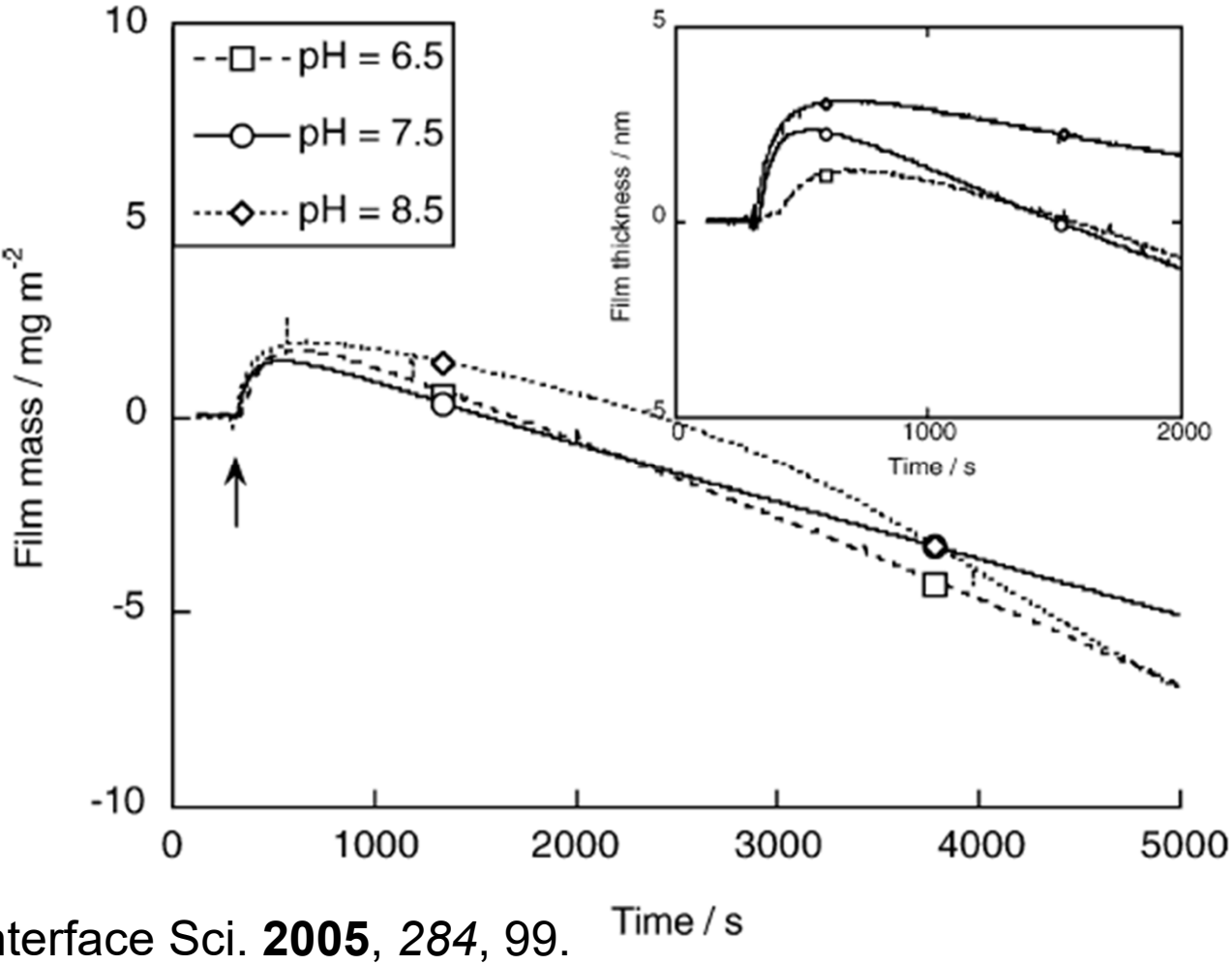
$$\Gamma = 3d_1 \frac{\frac{n_1 - n_0}{(n_1^2+2)(n_0^2+2)}}{\frac{A}{M} - v\frac{n_0^2-1}{n_0^2+2}}(n_1 - n_0).$$

Application example: *in situ* determination of enzyme activity

(1) The enzymes adsorb
→ increase in film mass

(2) The enzymes start to degrade cellulose
→ decrease in film mass

Effect of pH



J. Colloid Interface Sci. **2005**, *284*, 99.

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Application example: *in situ* determination of enzyme activity

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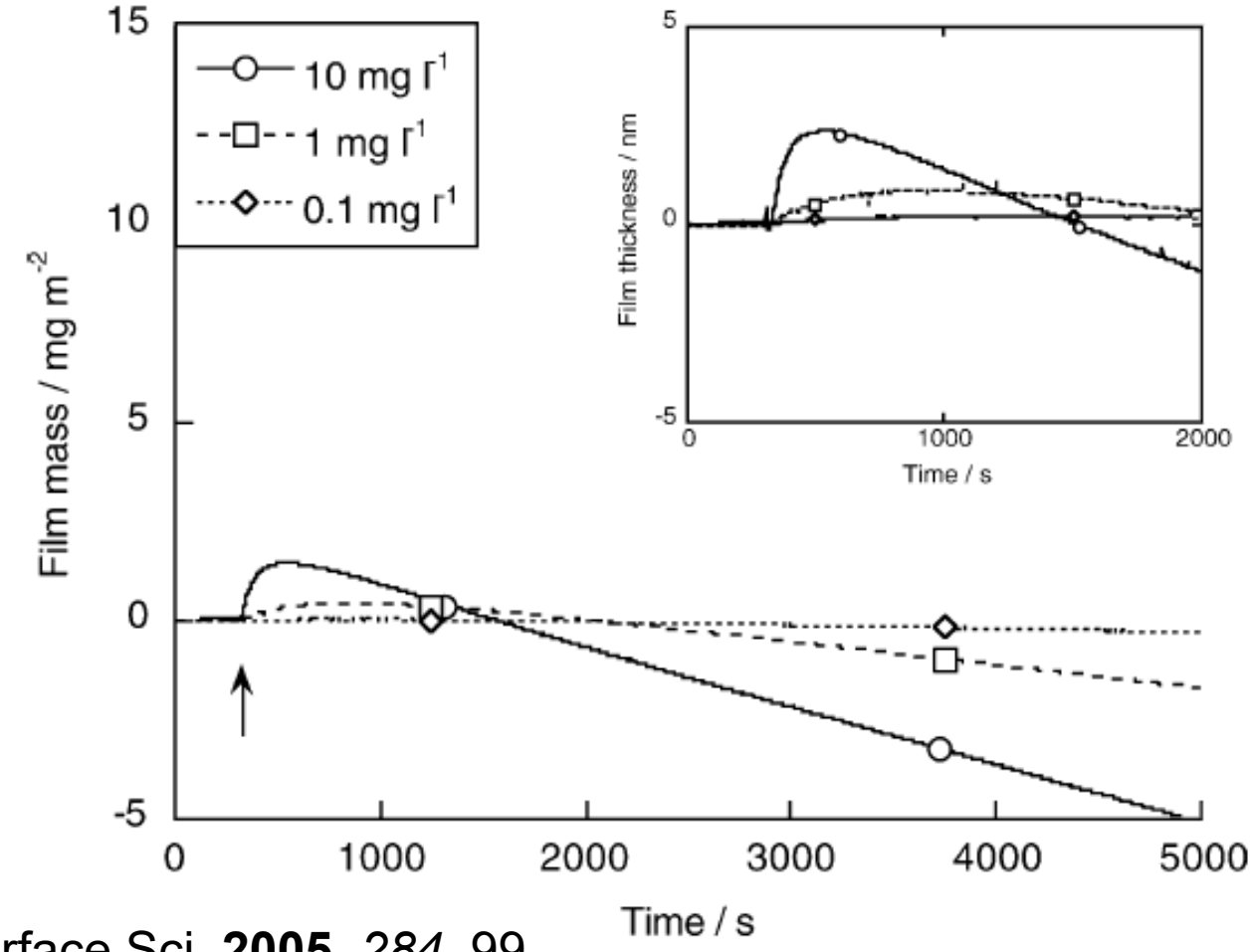
(2) The enzymes start to degrade cellulose
→ decrease in film mass

Effect of temperature



J. Colloid Interface Sci. **2005**, *284*, 99.

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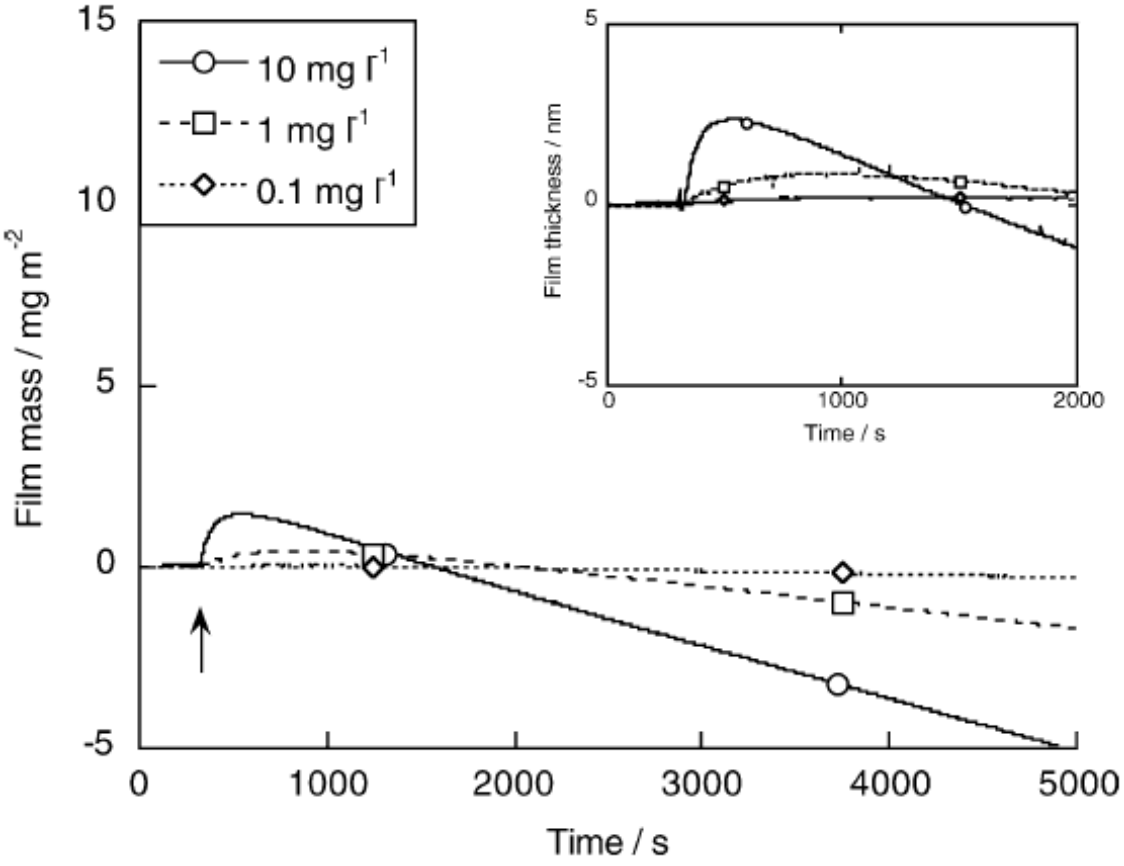
Application example: *in situ* determination of enzyme activity

(1) The enzymes adsorb
→ increase in film mass

(2) The enzymes start to degrade cellulose
→ decrease in film mass

Effect of enzyme concentration



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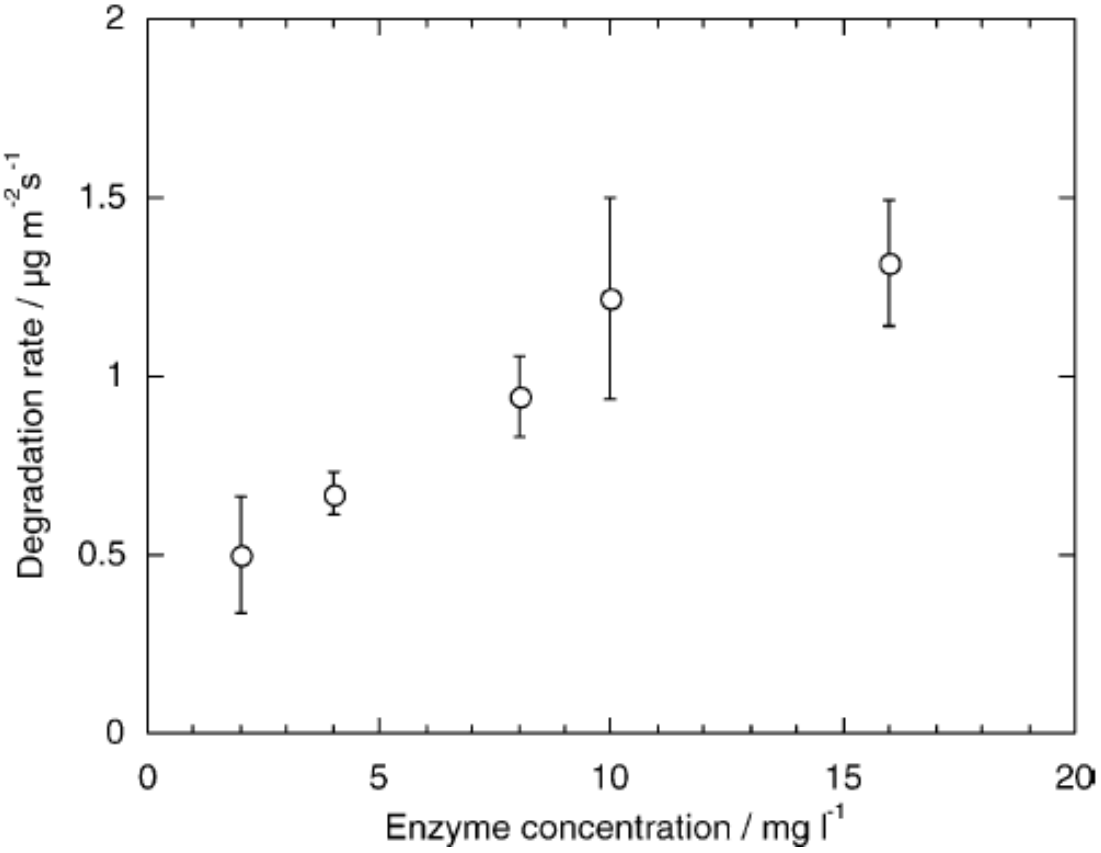
J. Colloid Interface Sci. **2005**, *284*, 99.

Application example: *in situ* determination of enzyme activity

With ellipsometry data, it is easy to calculate the degradation rate of cellulose exposed to the enzymes.



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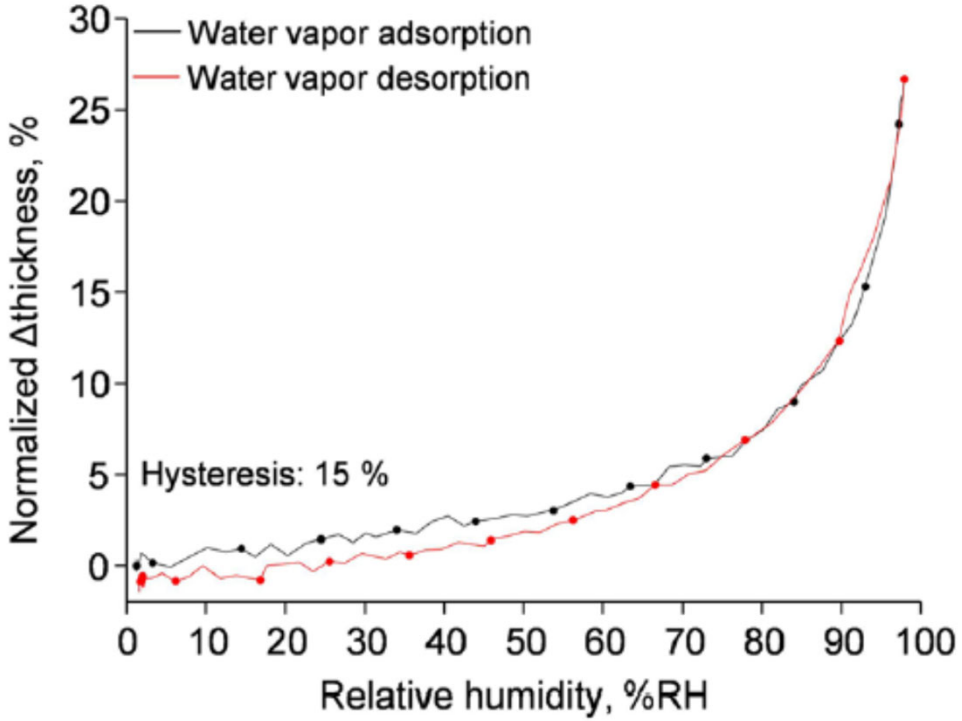
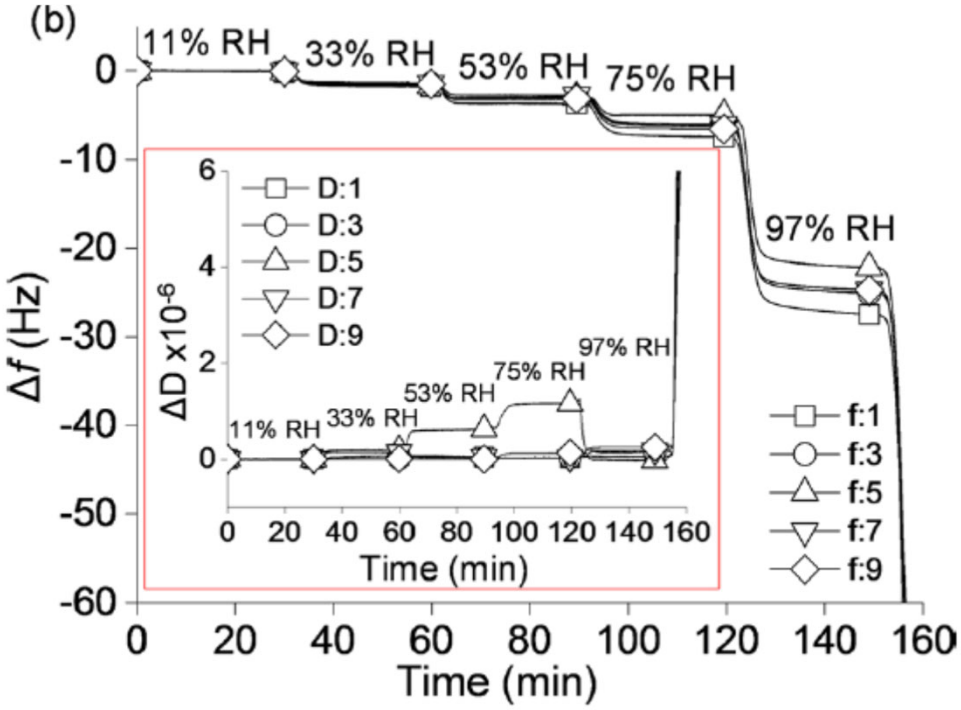
Application example: swelling of cellulose nanocrystal film in vapor

Spectroscopic ellipsometry: thickness change



Quartz crystal microbalance: mass change



Decrease in frequency
→ Increase in mass

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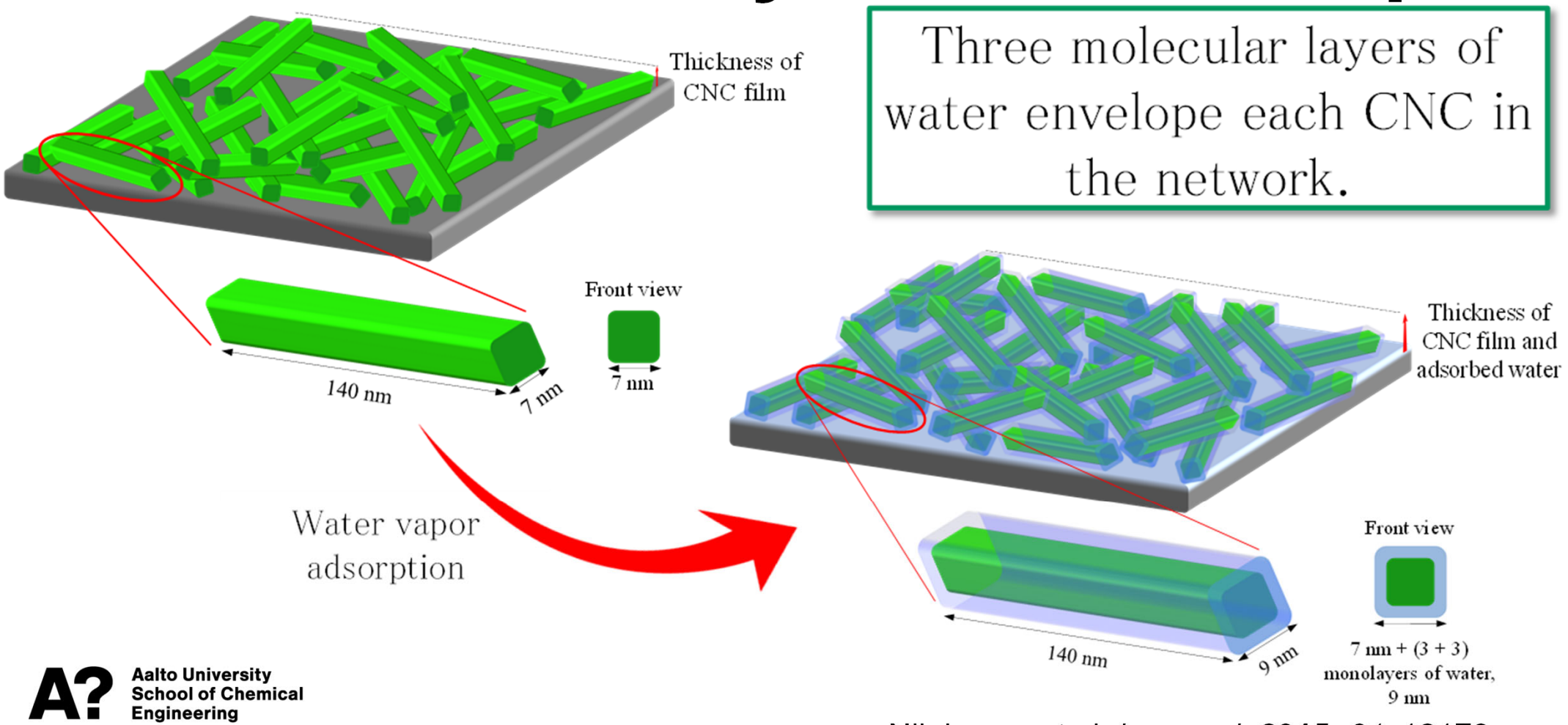
Application example: swelling of cellulose nanocrystal film in vapor



Three molecular layers of water envelope each CNC in the network.

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Niinivaara et al. *Langmuir* **2015**, *31*, 12170.

Note on adsorption and ellipsometry

- Because of ambiguities in interpretation and the scant availability of in situ setups, ellipsometry is not used very often in *in situ* adsorption studies
- QCM and SPR are nowadays for more common in solution-based adsorption studies
- Ellipsometry is a good complementary technique

X-ray reflectivity (XRR)

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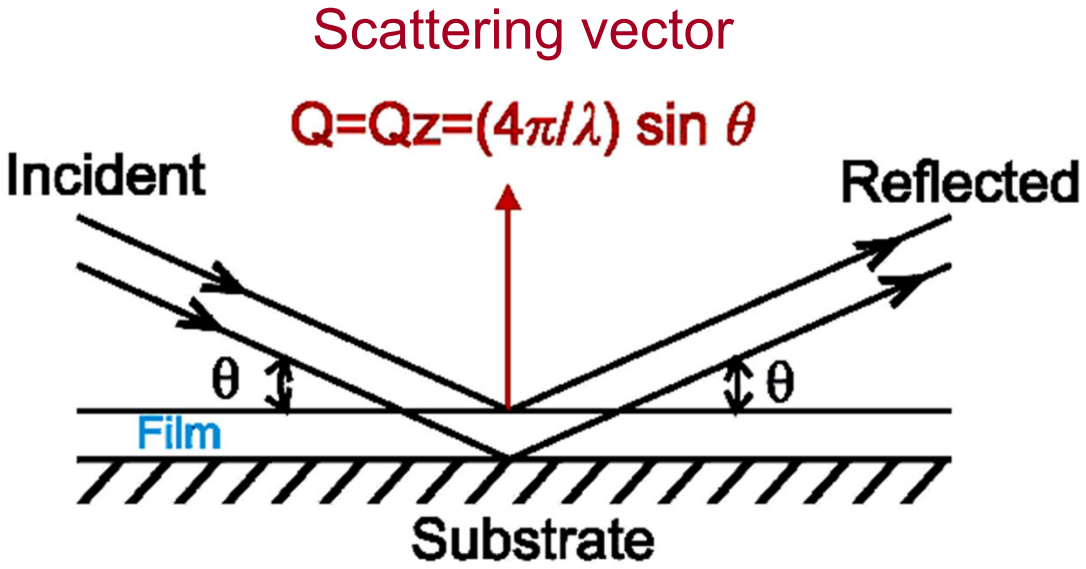
Theory

- Sample is exposed to monochromatic X-rays coming in at grazing angle
- The reflected intensity is plotted as a function of scattering vector (or reflection angle θ)



Reflectivity presents periodical oscillations in reciprocal space.
Reason: constructive interference at substrate-film and substrate-air interface.
Result: accurate determination of film thickness.

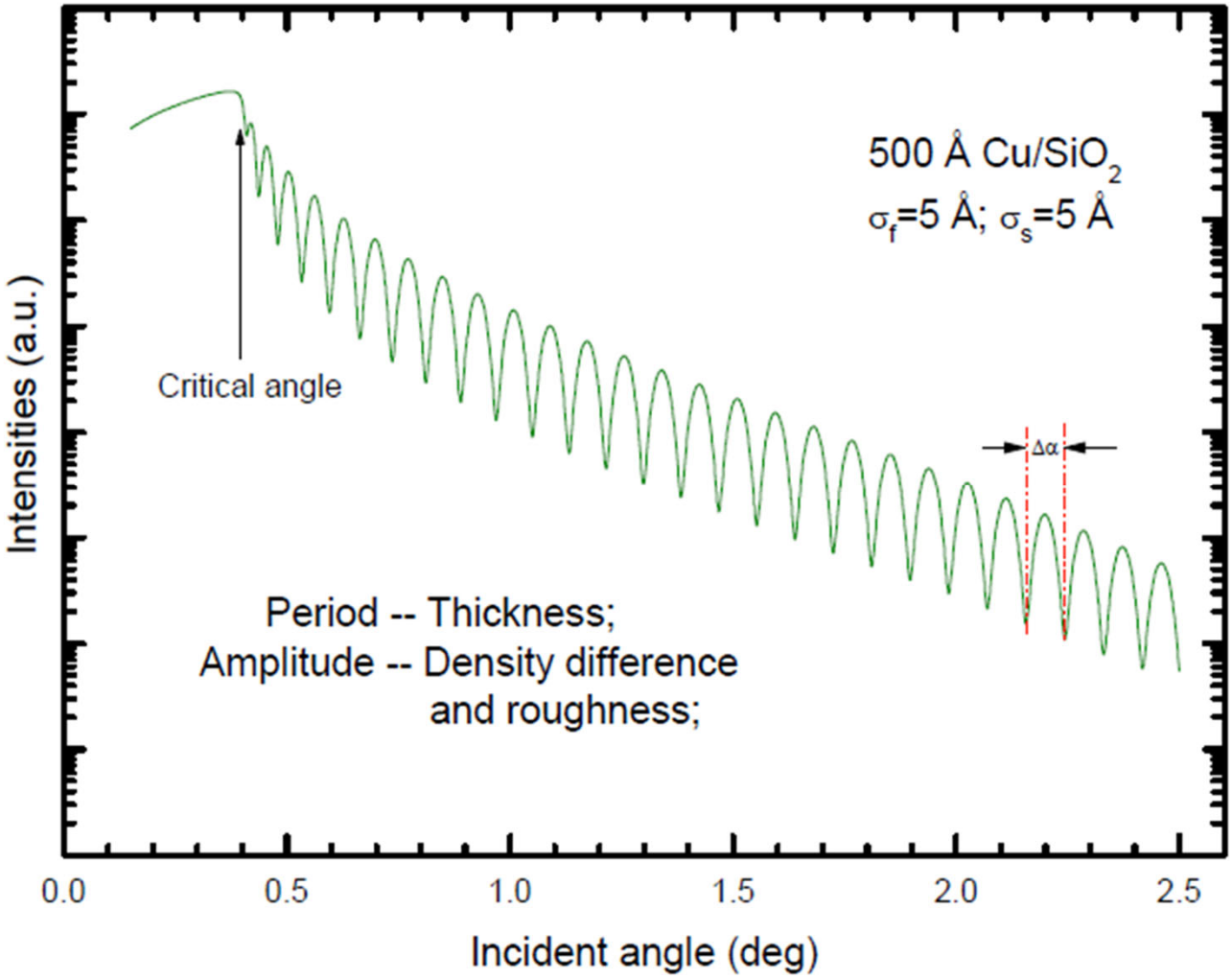
Theory

First, total reflection occurs with very small reflection angles.

After the **critical angle (α_c)**, interference fringes occur.

Note: the interference fringes are also called *Kiessig fringes*.

Example: 50 nm Cu film on silica (SiO_2)



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Theory

Complex refractive index:

$n = 1 - \delta - i\beta$

Note that refraction depends also on mass density of the film.

$$\delta = \left(\frac{2\pi}{k_0^{\,2}}\right) r_e N_a \rho \left(\frac{Z + f'}{M_a}\right)$$

$$\beta = \left(\frac{2\pi}{k_0^{\,2}}\right) r_e N_a \rho \left(\frac{f''}{M_a}\right)$$

$k_0 = 2\pi/\lambda$ (with λ being the wavelength) is the length of the x-ray wave vector
r_e is the classical electron radius
N_a is Avogadro's number
ρ is the mass density
Z is the atomic number
M_a is the atomic mass
f' is the real part of the dispersion coefficient
f'' is the imaginary parts of the dispersion coefficient

Theory

Reflectance coefficient (R_F):

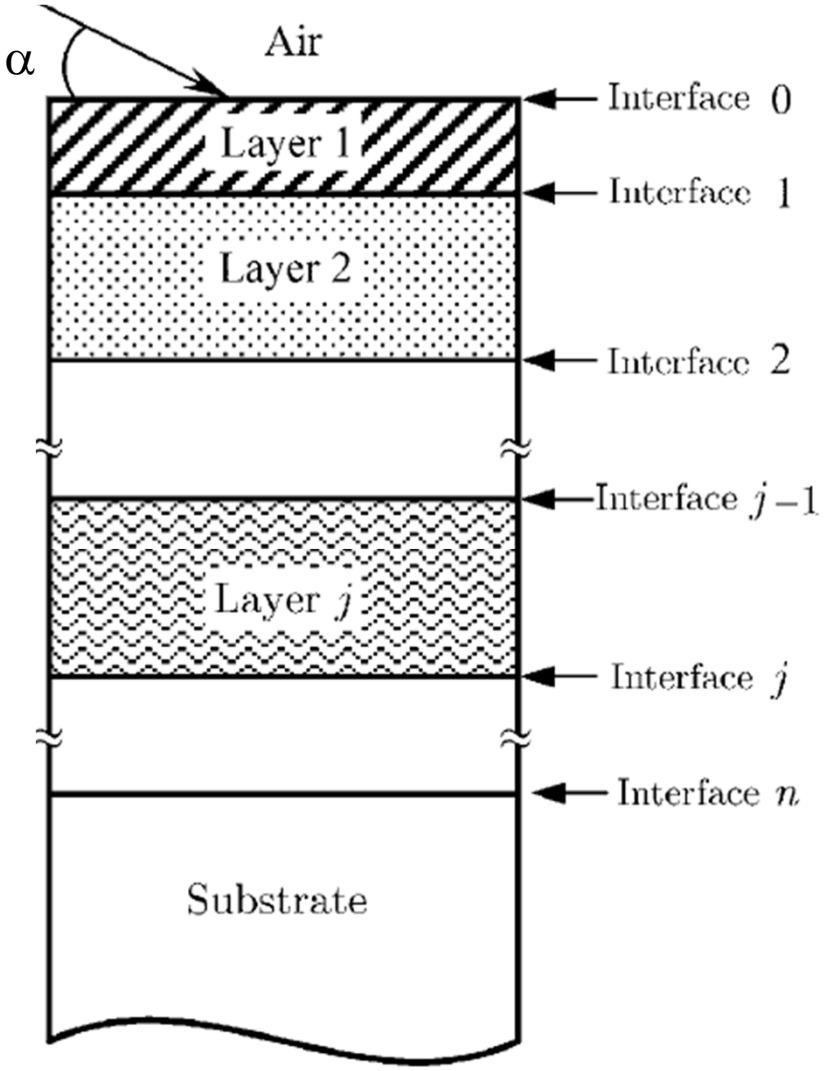
$$R_F = \left| \frac{r_0^{N-C} F_0 + r_1^{N-C} F_1 \exp(-i2k_0 f_1 h)}{1 + r_0^{N-C} r_1^{N-C} F_0 F_1 \exp(-i2k_0 f_1 h)} \right|^2 = \left| \frac{R_F'}{R_F''} \right|$$

h – film **thickness**

$$r_j^{N-C} = \exp(-2k_0^2 \sigma_j^2 f_j f_{j+1})$$

Roughness factor

$$F_j = \frac{f_j - f_{j+1}}{f_j + f_{j+1}}$$



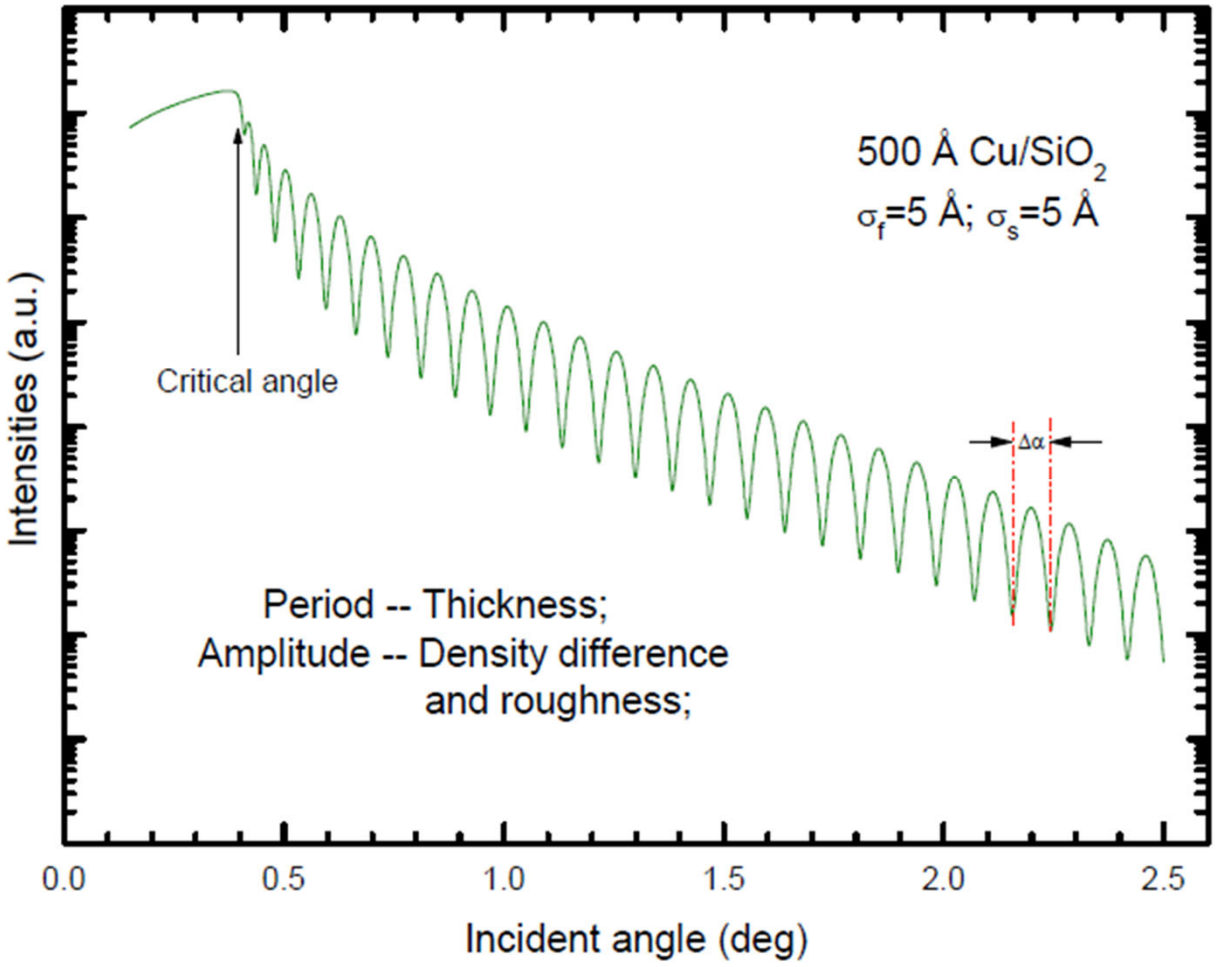
$$f_j = \sqrt{\alpha^2 - 2\delta_j - i2\beta_j}$$

Dependence on incident angle and complex refractive index (incl. mass **density**)

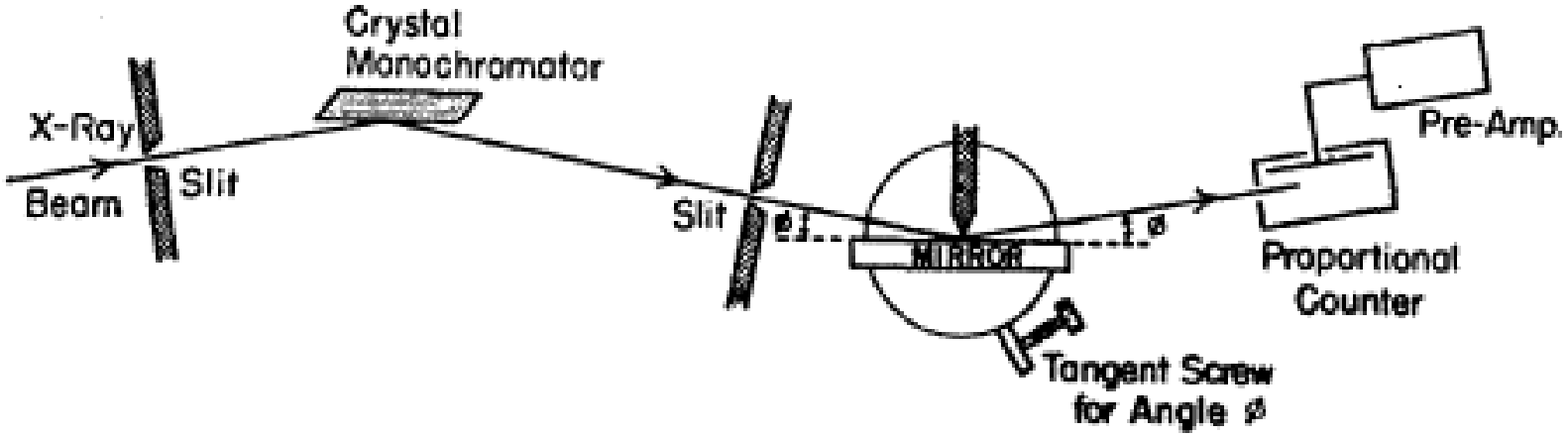
Theory

Overall, the determining factors for the reflectivity curve are:

- film thickness
- film roughness
- mass density of the film



Instrumentation



- Angle of incidence is varied manually during the measurement
- The sample area should be maximized
- XRR is usually feasible to operate with an X-ray diffractometer

Phys. Rev. **1954**, *95*, 359.

Instrumentation

- X-ray reflectivity may also be performed at a synchrotron facility (particle accelerator that produces an x-ray beam of unusual intensity)

- Synchrotron sources are expensive and laborious to use but the data quality is excellent

Interpretation of data

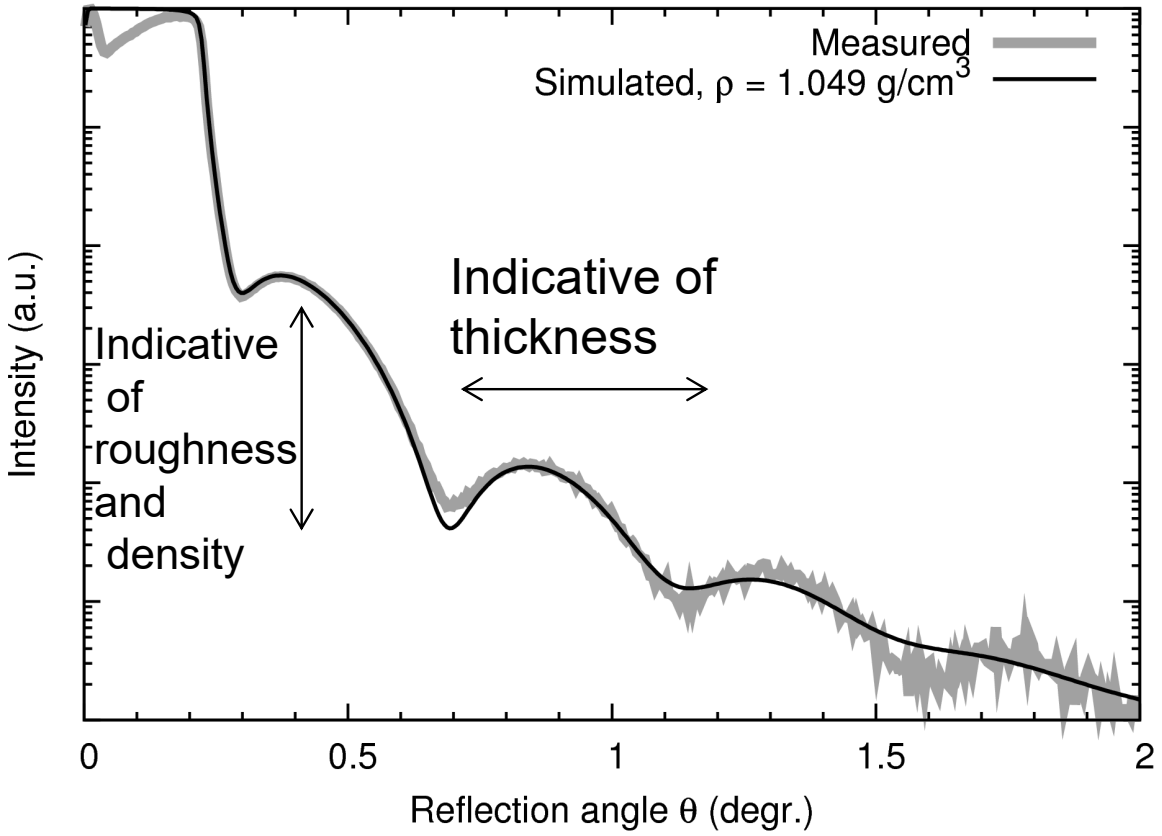
- Like ellipsometry, XRR is an indirect method
- Reflected intensity does not yield any concrete physical information on the sample
- Modelling is required to yield actual physical values

→ One must iterate values for thickness, density, and n roughness which would give a reasonable fit to the measurement values

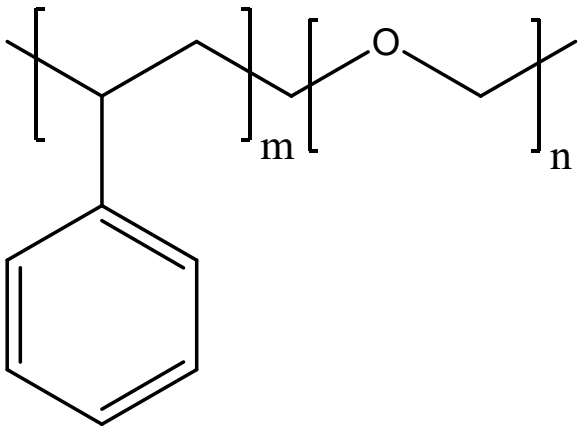
→ Values for film **thickness, density, and roughness**

- In general, the values for film thickness are highly reliable, but the values for mass density are less reliable, particularly with soft materials

Example of simulating the reflectivity curve



Polystyrene-*block*-polyethyleneoxide



Thickness: 9.9 nm
Roughness: 1.8 nm
Density: 1.05 g cm^{-3}

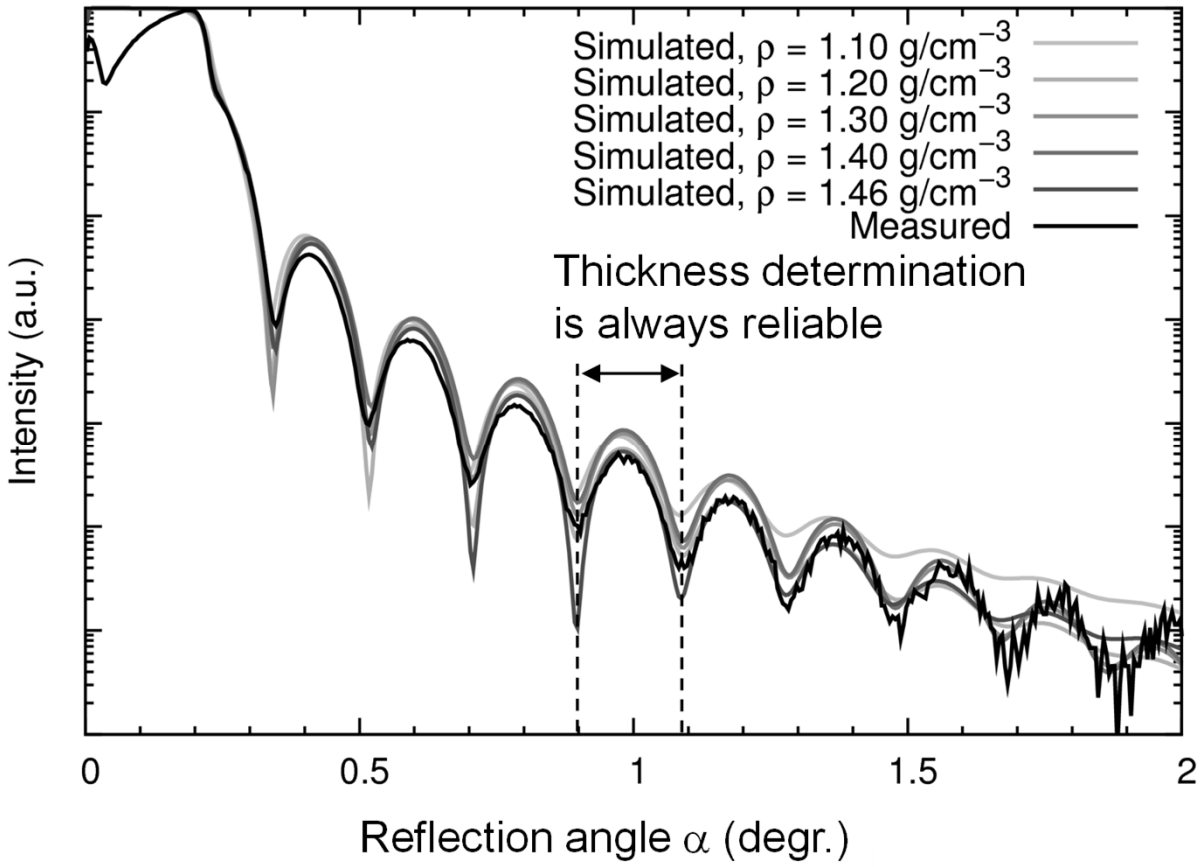
Mass density of organic thin films

PROBLEM WITH SOFT MATERIALS IN DENSITY APPROXIMATION

Different density values yield very similar fits.

↳ **UNRELIABLE**

XRR profile of 20 nm cellulose film



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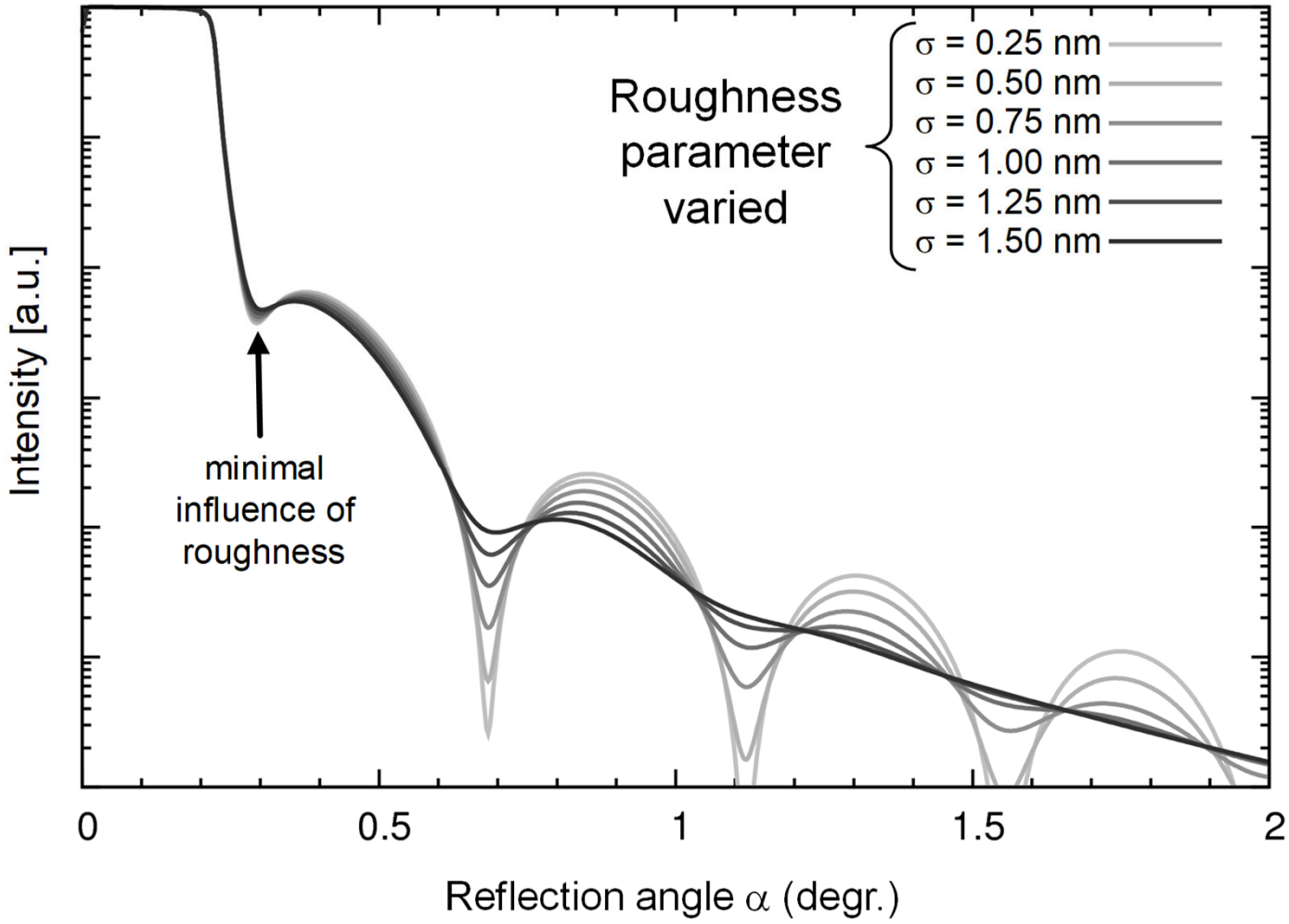
Why the density fit is unreliable

Thickness = 10 nm
density of polystyrene
~1.05

Roughness affects the positions of local minima more than density does.

Simulated XRR curve of polystyrene-like material



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Can the density fit be reliable?

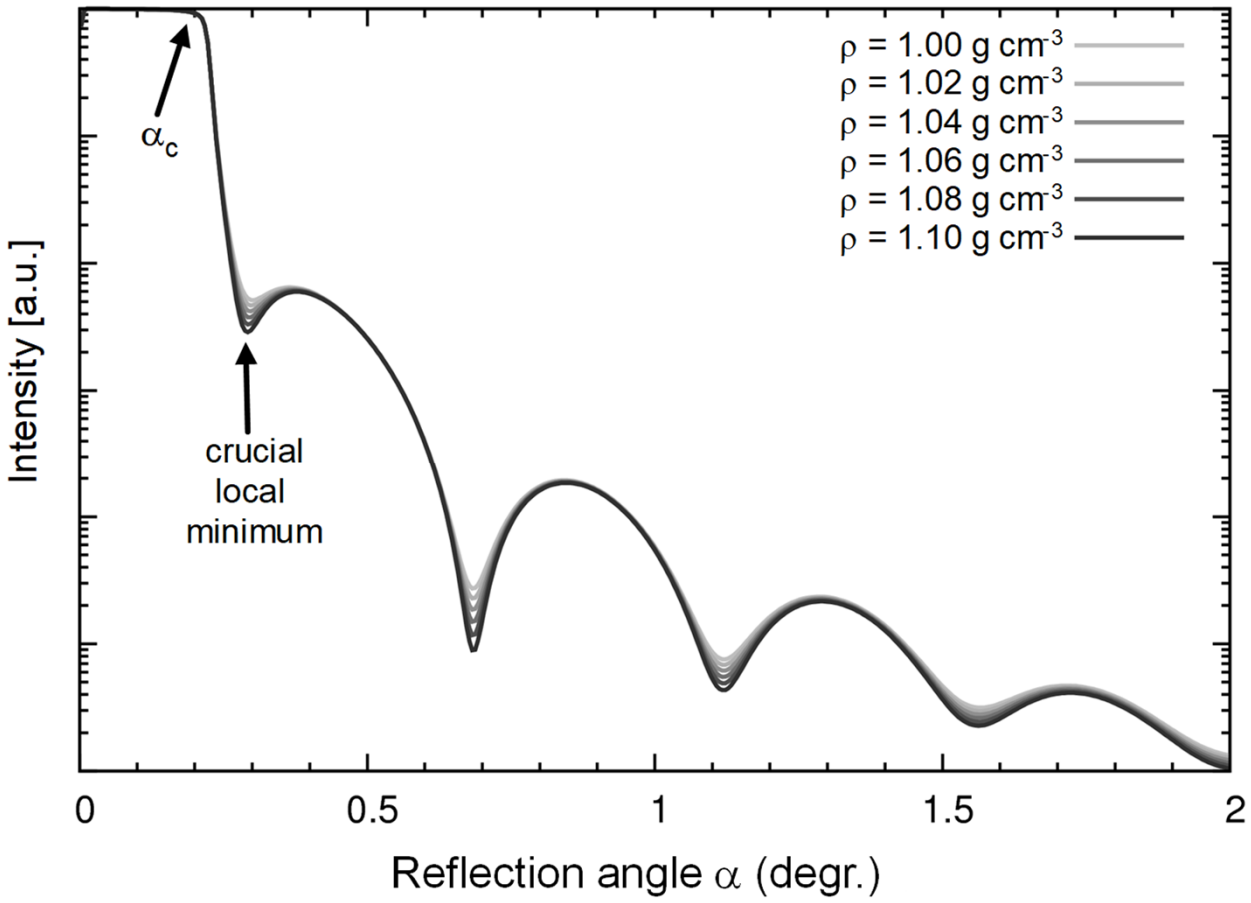
DISCOVERY: DENSITY DETERMINATION RELIABLE AT CERTAIN FILM THICKNESS VALUES (e.g. 5-17 nm)

In ca. 10 nm films,
small changes in density
parameter yield
already different fits.

↕

Reliable density determination
at 5-17 nm film thickness.

XRR profile of 10 nm polystyrene film



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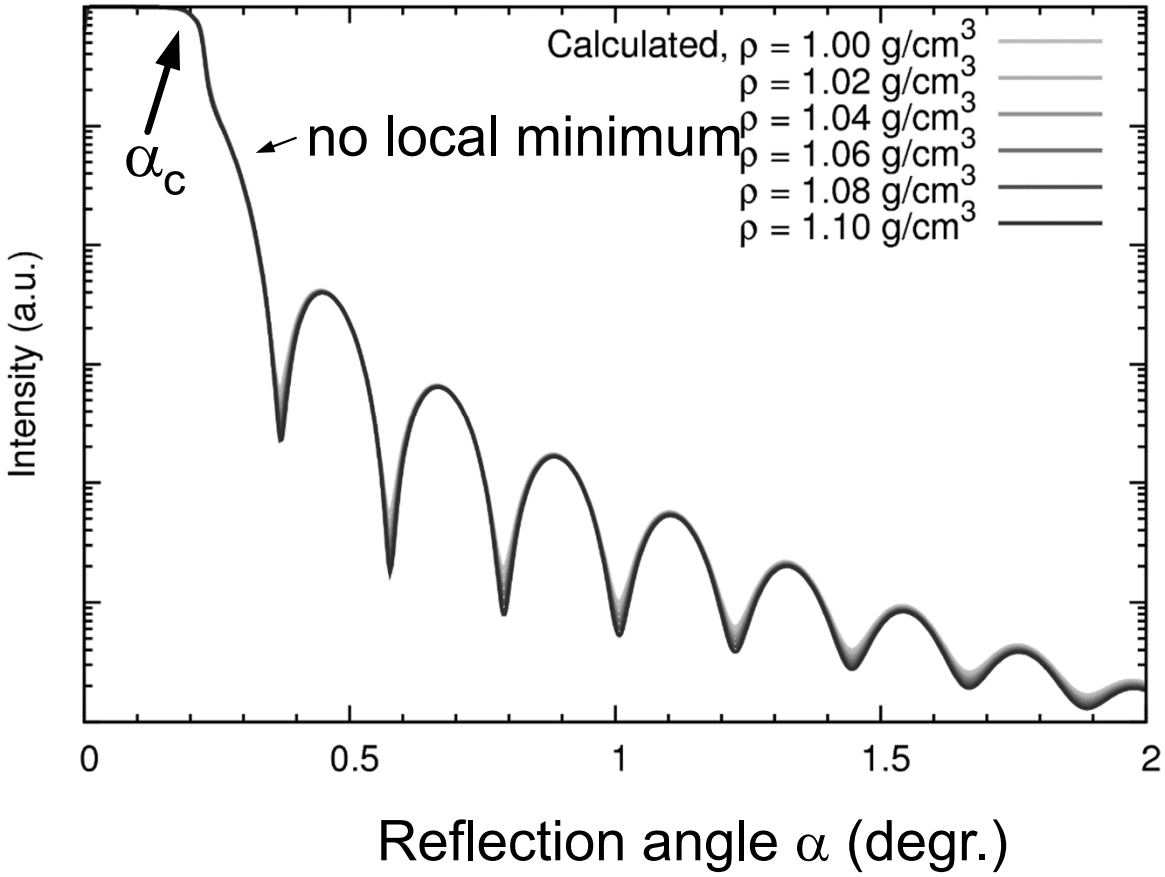
Can the density fit be reliable?

DISCOVERY: DENSITY DETERMINATION UNRELIABLE AT MANY THICKNESS VALUES (e.g. 20-40 nm)

Local minimum just next to α_c must be present – otherwise the density determination is unreliable.

XRR profile of 20 nm polystyrene film



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Experimental data on density

Sample	*Thickness [nm]*	*Roughness [nm]*	*Density [g cm^{-3}]*	**Density in bulk [g cm^{-3}]**
Polystyrene	15.0	0.39	1.03	1.047[a]
Poly(methyl methacrylate)	16.4	0.62	1.15	1.188[a]
Polystyrene-*block*-polyethyleneoxide	9.9	1.18	1.05	1.065[b]
Cellulose	6.7	0.52	1.51	1.52[c]
Trimethylsilyl cellulose	14.7	0.55	0.99	n.a.
Carboxymethyl cellulose	17.0	0.15	1.56	1.59[a]

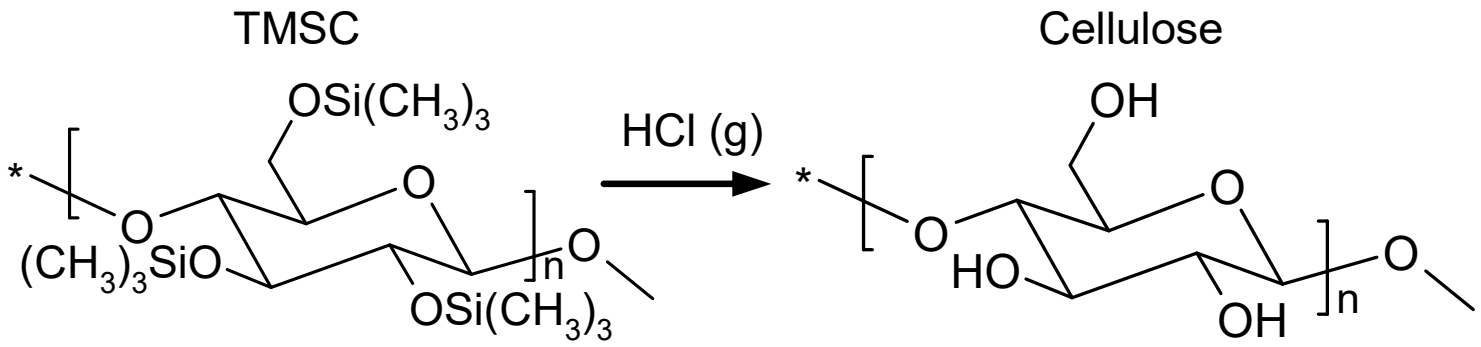
→ Reasonable correlation with bulk values

Application example: following reaction kinetics in ultrathin film

From XRR data: - thickness
- density

➡ **Molar mass**

Example: Hydrolysis of trimethylsilyl cellulose (TMSC) to cellulose



With 0.5 M HCl, the reaction spans ~10 min.

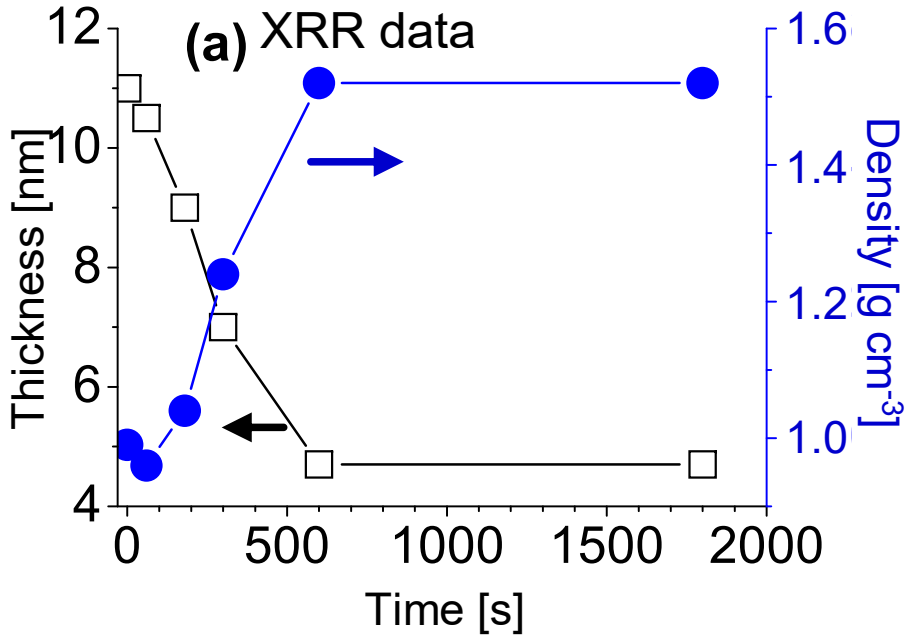
Reaction kinetics with XRR

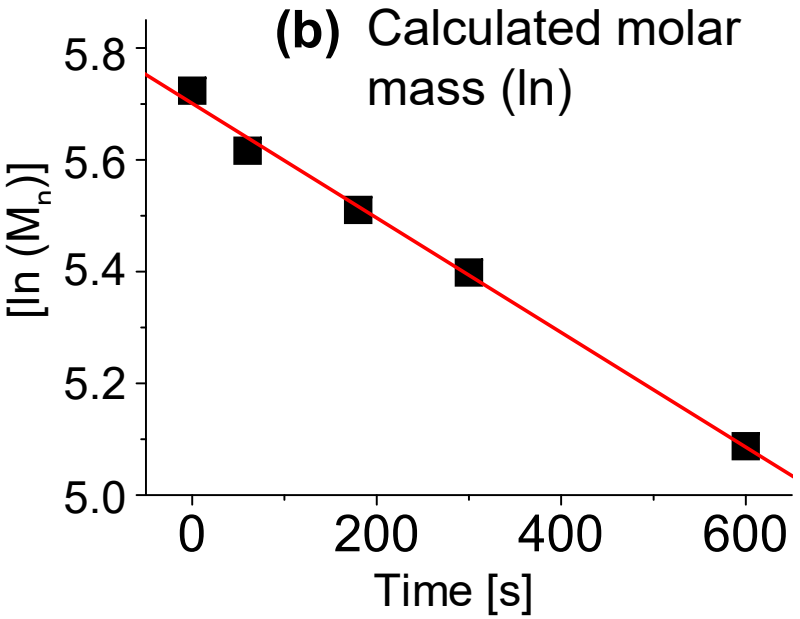
$$M_n = M_0 - \frac{h_0 d_0 - h_n d_n}{h_0 d_0 - h_k d_k}(M_0 - M_k)$$

M_0 is the molar mass of the starting material
M_k is the molar mass of the final material
h_0 is the initial film thickness,
d_0 is the initial mass density of the film
h_k is the final film thickness,
d_k is the final density of the film
h_n is the film thickness at a certain point of the reaction
d_n is the mass density of the film at a certain point of the reaction

Reaction kinetics with XRR

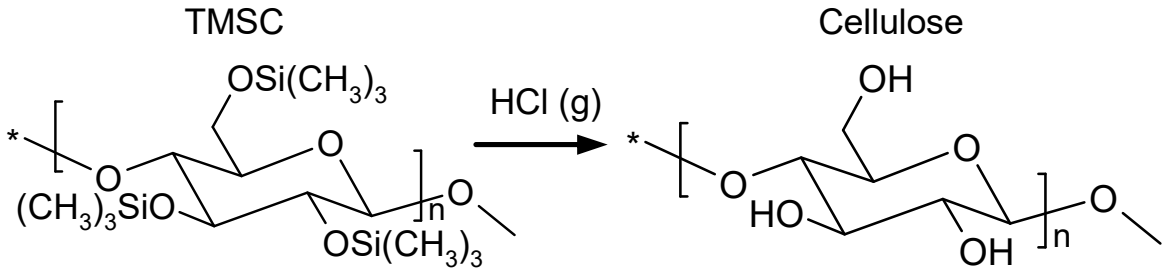
Hydrolysis of TMSC to cellulose with 0.5 M HCl was followed at RT





First order reaction

$K=1.2\times10^{-3}\ s^{-1}$



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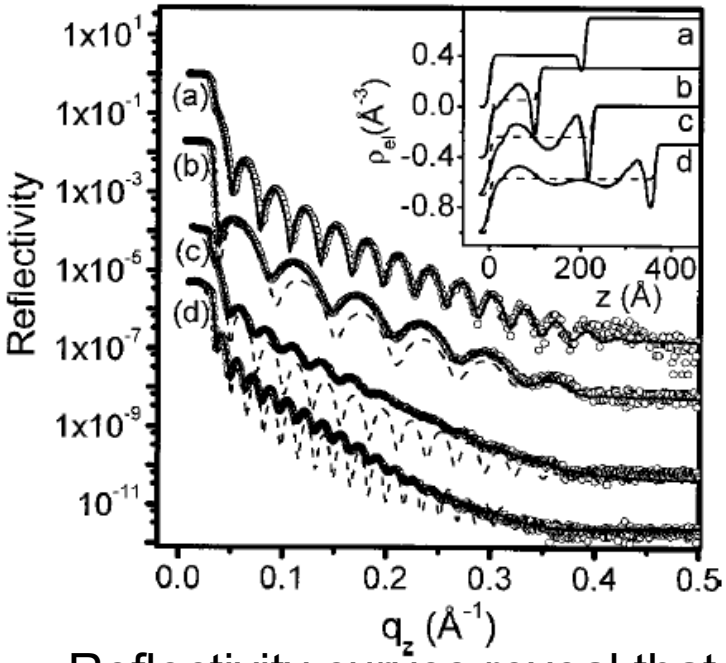
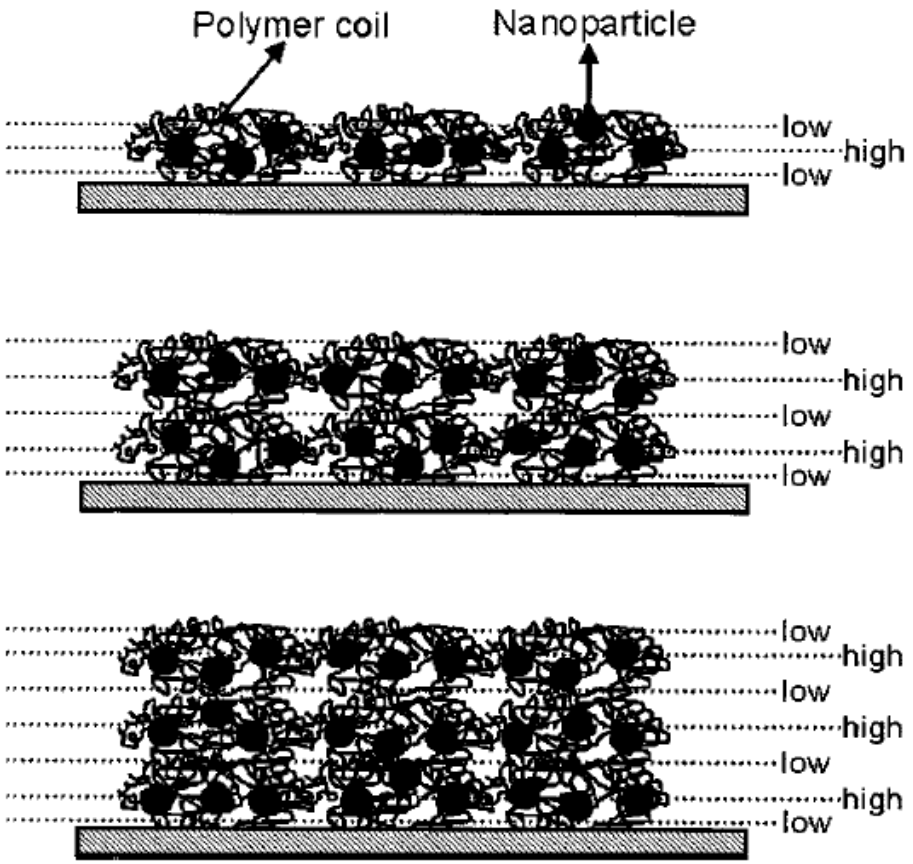
J. Am. Chem. Soc. **2010**, *132*, 3678.

Application example: ordered nanocomposites





Reflectivity curves reveal that polyacrylamide spin coated with CdS nanoparticles to an ultrathin film is an ordered nanocomposite (discrete layers).

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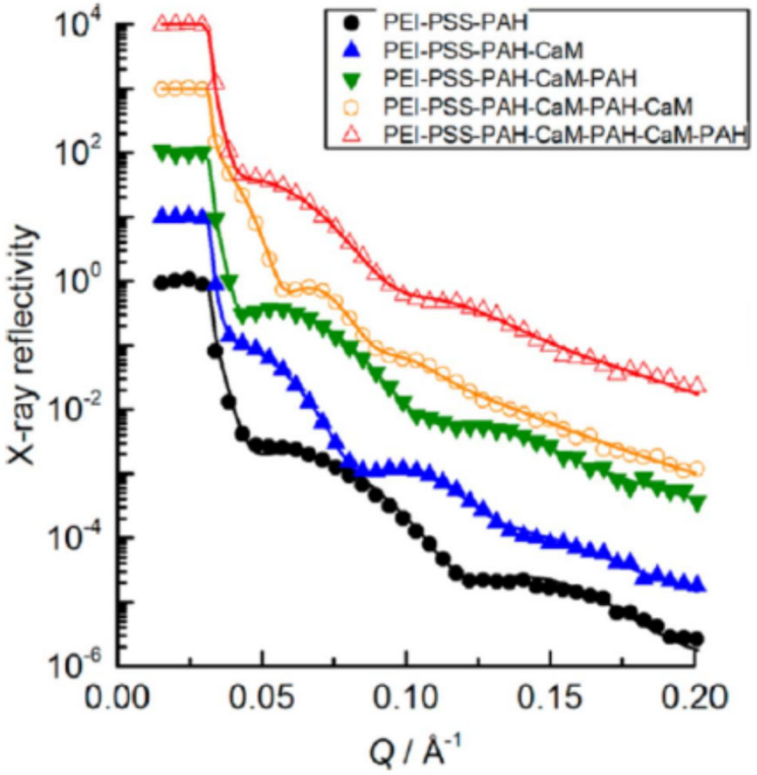
Phys. Rev. E **2004**, *70*, 051608.

Application: Layer-by-layer films with polymers



Protein called calmodulin (CaM) is mixed in an LbL film of cationic (PEI, PAH) and anionic (PSS) polyelectrolytes

multilayer	d/Å
PEI-PSS-PAH	79
PEI-PSS-PAH-CaM	116
PEI-PSS-PAH-CaM-PAH	89
PEI-PSS-PAH-CaM-PAH-CaM	173
PEI-PSS-PAH-CaM-PAH-CaM-PAH	96

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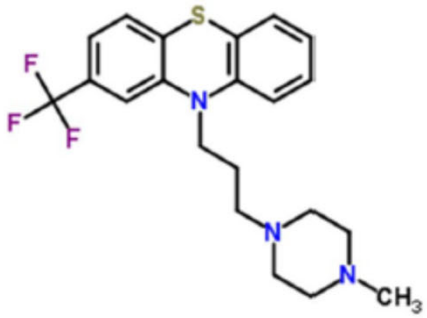
Langmuir **2017**, *33*, 3982.

Application: Layer-by-layer films with polymers

- Layer thickness values within the multilayers are probed by XRR
- It turns out CaM thickness inside the multilayer is very little affected by trifluoperazine (TFP), a ligand that changes CaM conformation in bulk

deposition unit	Δd/Å by XR
PEI-PSS-PAH	+62 ± 14 (23)
PEI-(PSS-PAH)$_2$	
first CaM	+50 ± 21 (7)
first CaM(TFP)	+49 ± 18 (11)
second CaM	+87 ± 15 (3)
second CaM(TFP)	+74 ± 8 (3)
CaM-PAH	+14 ± 7 (17)[c]



Langmuir **2017**, *33*, 3982.

Summary

- Ellipsometry and XRR are both based on electromagnetic radiation reflecting from a substrate of an ultrathin film
- Both yield data for film thickness with excellent accuracy
- With ellipsometry, it helps if you know the refractive index of the material; with XRR you don’t need any preliminary information of the sample
- XRR gives you roughness and density of the film with precautions
- An XRR measurement is generally slower than spectroscopic ellipsometry; it is therefore not used often as an *in situ* technique
- Both are extensively used for film thickness characterization